A Variational Procedure For Improving The Born Approximation As Applied To The Scattering Of Electrons By Hydrogen Atoms

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

I. INTRODUCTION

In the application of wave mechanics to the calculation of the scattering of electrons by atoms, the simplest problem which can be treated is the collision of electrons with hydrogen atoms since the complete set of hydrogen eigenfunctions is available. Hence, any method proposed for treating electron-atom scattering problems must first be shown to be successful when applied to the hydrogen atom.

The wave function $\Psi(\vec{r}_1, \vec{r}_2)$ which describes the scattering of an electron incident on a hydrogen atom in the ground state must satisfy the wave equation[1]

$$\left[(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) + E + (e^2/r_1) + (e^2/r_2) - (e^2/r_{12}) \right] \Psi = 0. \quad (1)$$

where r_1, r_2, and r_{12} are the respective distances of the two electrons from the nucleus and each other. The mass of the electron is small enough compared to that of the proton so that the motion of the proton in the collision may be neglected. The total energy E of the system is the sum of the energy E_0 of the atomic electron in the ground state and of the kinetic energy $mv^2/2$ of the incident electron. The

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[1] N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions (Clarendon Press, Oxford, 1949), second edition: Chap. VIII, section 2. This treatise on scattering problems gives a complete up-to-date account of most of the work done on this problem.

wave function $\Psi(\vec{r}_1, \vec{r}_2)$ must remain finite as r_1 and r_2 approach zero, and for large r_1 and r_2 it must have the asymptotic form

$$\Psi_o \rightarrow \psi_o(\vec{r}_1) \exp(ik_o \vec{n} \cdot \vec{r}_2) + (1/r_2) \sum_m \psi_m(\vec{r}_1) f_{mo}(\vec{n}; \vec{n}_2) \times$$

$$\exp(ik_m r_2),$$

$$\text{as } r_2 \rightarrow \infty ; \tag{2a}$$

$$\Psi_o \rightarrow (1/r_1) \sum_m \psi_m(\vec{r}_2) g_{mo}(\vec{n}; \vec{n}_1) \exp(ik_m r_1),$$

$$\text{as } r_1 \rightarrow \infty, \tag{2b}$$

where $\psi_m(\vec{r})$ is a member, with energy E_m, of the orthonormal set of hydrogen eigenfunctions; $k_m^2 = (2m/\hbar^2)(E - E_m)$; $\vec{n}$ is a unit vector in the direction of the incident electron and of unspecified orientation; $\vec{n}_1$ and $\vec{n}_2$ are unit vectors having the spatial orientations of $\vec{r}_1$ and $\vec{r}_2$ respectively; f_{mo} and g_{mo} are respectively the scattering amplitude and "exchange" scattering amplitude associated with the $o \rightarrow m$ transition.

The a priori symmetry condition imposed on the total wave function for particles with half integral spin requires that the space wave function be either symmetric or antisymmetric in the coordinates of the two electrons to correspond, respectively, with antisymmetric (spin = 0) or symmetric (spin = 1) spin functions such that the total wave function is always antisymmetric. The total space wave functions

are then

$$\Psi_0(\vec{r}_1, \vec{r}_2) \pm \Psi_0(\vec{r}_2, \vec{r}_1) \qquad (3)$$

which have the asymptotic forms for large r_2

$$\psi_0(\vec{r}_1)\exp(ik_0\vec{n}\cdot\vec{r}_2) + (1/r_2) \sum_m \left[f_{mo}(\vec{n};\vec{n}_2) \right.$$

$$\left. \pm g_{mo}(\vec{n};\vec{n}_2) \right] \exp(ik_0 r_2) \; \psi_m(\vec{r}_1) \qquad (4a)$$

and for large r_1

$$\pm \psi_0(\vec{r}_2)\exp(ik_0\vec{n}\cdot\vec{r}_1) + (1/r_1) \sum_m \left[g_{mo}(\vec{n};\vec{n}_1) \right.$$

$$\left. \pm f_{mo}(\vec{n};\vec{n}_1) \right] \exp(ik_0 r_1) \; \psi_m(\vec{r}_2). \qquad (4b)$$

For calculation purposes, it is assumed that the intensity of the beam of electrons falling on a hydrogen atom initially in the normal state is such that one electron crosses unit area per unit time. The scattering of the electrons from a beam of unit intensity is measured in terms of the differential cross section $I(\theta,\phi)$ dw, defined as the number of electrons which fall per unit time on an area dS (dS = r^2dw) placed at a large distance r from the scattering atom. For the o→m transition, the differential cross section $I_{mo}(\theta,\phi)$dw is the sum of the number of electrons which, after exciting the state m in the atom, are scattered into the solid angle dw located at (θ, ϕ) in unit time and the number of electrons which, after the incident electrons have been

captured into the state m of the atom, are ejected into the same solid angle dw in unit time. Thus from either Eq. (4a) or Eq. (4b) we have

$$I_{mo}(\theta\phi) \, dw = (k_m/k_o)\left[3/4|f_{mo} - g_{mo}|^2 + 1/4|f_{mo} - g_{mo}|^2\right] dw \quad (5)$$

since the probabilities of the electrons having parallel spins and of the electrons having anti-parallel spins are in a ratio of 3 to 1.[2] In order to obtain the scattering cross sections, the values of the scattering amplitudes f_{mo} and g_{mo} must be obtained.

Returning to the wave equation (1), we rearrange the equation and multiply through by $\psi_o^*(\vec{r}_1)$:

$$(\hbar^2/2m) \, (\nabla_2^2 + k_o^2) \, \psi_o^*(\vec{r}_1)\Psi(\vec{r}_1, \vec{r}_2) = \psi_o^*(\vec{r}_1)\left[(-\hbar^2/2m)\nabla_1^2 - E_o\right.$$

$$\left.-(e^2/r_1)\right]\Psi(\vec{r}_1, \vec{r}_2) - \left[(e^2/r_2) - (e^2/r_{12})\right] \psi_o^*(\vec{r}_1)\Psi(\vec{r}_1, \vec{r}_2) . \quad (6)$$

Since

$$\left[(-\hbar^2/2m)\nabla_1^2 - (e^2/r_1)\right] \psi_o(\vec{r}_1) = E_o \, \psi_o(\vec{r}_1), \quad (7)$$

the integration of Eq. (6) reduces <u>via</u> Green's Theorem to

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[2] <u>Ibid.</u>, Chap. V.

$$(\hbar^2/2m)\left[\nabla_2^2 + k_0^2\right]\int \psi_0^*(\vec{r}_1)\Psi(\vec{r}_1,\vec{r}_2)d\tau_1 =$$
$$-\int\left[(e^2/r_2) - (e^2/r_{12})\right]\psi_0^*(\vec{r}_1)\Psi(\vec{r}_1,\vec{r}_2)d\tau_1. \qquad (8)$$

If we define a function

$$F_0(\vec{r}_2) = \int \psi_0^*(\vec{r}_1)\Psi(\vec{r}_1,\vec{r}_2)d\tau_1, \qquad (9)$$

it follows from (8) that

$$(\hbar^2/2m)\left[\nabla_2^2 + k_0^2\right]F_0(\vec{r}_2) = -\int\left[(e^2/r_2) - (e^2/r_{12})\right] \times$$
$$\psi_0^*(\vec{r}_1)\Psi(\vec{r}_1,\vec{r}_2)d\tau_1$$
$$\equiv \Phi_0(\vec{r}_2,\vec{n}). \qquad (10)$$

The solution $F_0(\vec{r}_2)$ of this integro-differential equation has the asymptotic form

$$F_0(\vec{r}_2) \rightarrow \exp(ik_0\vec{n}\cdot\vec{r}_2) + f_{00}\exp(ik_0 r_2)/r_2 \qquad (11)$$

as follows from Eqs. (9), (2). The required solution is[3]

$$F_0(\vec{r}_2) = \exp(ik_0\vec{n}\cdot\vec{r}_2) - (2m/4\pi\hbar^2) \times$$
$$\int\left[\exp(ik_0|\vec{r}_2 - \vec{r}'|)/|\vec{r}_2 - \vec{r}'|\right]\Phi_0(\vec{r}',\vec{n})d\tau'. \qquad (12)$$

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[3] Ibid., Chap. VI.

with, as a result,

$$f_{oo}(\vec{n}, \vec{n}') = (2m/\hbar^2)\int \exp(-ik_o \vec{n}' \cdot \vec{r}') \; \overset{\Phi}{\Phi}_0(\vec{r}', \vec{n}) d\tau', \qquad (13)$$

as follows from (11). Eq. (10) is only one of a set of simultaneous integro-differential equations for the functions

$$F_n(\vec{r}_2) = \int \psi_n^*(\vec{r}_1) \Psi(\vec{r}_1, \vec{r}_2) d\tau_1. \qquad (14)$$

By the same method, an integral equation of the form (13) can be found for the scattering amplitude f_{no} corresponding to each function $F_n(\vec{r}_2)$:

$$f_{no}(\vec{n}, \vec{n}') = (2m/\hbar^2)\int \exp(-ik_n \vec{n}' \cdot \vec{r}') \; \overset{\Phi}{\Phi}_n(\vec{r}', \vec{n}) d\tau'. \qquad (15)$$

Similarly, for the set of functions

$$G_n(\vec{r}_1) = \int \psi_n^*(\vec{r}_2) \Psi(\vec{r}_1, \vec{r}_2) d\tau_2, \qquad (16)$$

we have a set of simultaneous integro-differential equations corresponding to (10)

$$(\hbar^2/2m)(\nabla_1^2 + k_n^2) G_n(\vec{r}_1) = -\int \left[(e^2/r_1) \right.$$
$$\left. - (e^2/r_{12}) \right] \psi_n^*(\vec{r}_2) \Psi(\vec{r}_1, \vec{r}_2) d\tau_2$$
$$\equiv \chi_n(\vec{r}_1, \vec{n}), \qquad (17)$$

whose solutions yield [cf. (13)]

$$g_{no}(\vec{a}, \vec{a}') = (2m/\hbar^2) \int \exp(-ik_n \vec{a}' \cdot \vec{r}') \chi_n(\vec{r}', \vec{a}) d\tau'. \quad (18)$$

These integral equations (15), (18) for the scattering amplitudes f_{no} and g_{no} are exact, and since the exact solutions cannot be carried out by any reasonable method, various approximate solutions have been based on them.

Before proceeding further we simplify our considerations by restricting the problem to elastic scattering at relatively high velocities of impact.

The simplest approximation is that due to Born.[4] For high velocities of impact, the perturbation of the incident wave by its interaction with the atom will be small. Under these circumstances, Born takes as a zero-order approximation for Ψ, [cf. (2)]

$$\Psi(\vec{r}_1, \vec{r}_2) = \exp(ik_0 \vec{a} \cdot \vec{r}_2) \ \psi_o(\vec{r}_1), \quad (19)$$

which assumes that the incident electron is unaffected by the atomic field. Substituting (19) into the right-hand side of (10), and following the calculations through Eq. (13), the Born formula for the elastic scattering amplitude is given by

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[4]M. Born, Zeits. f. Physik 38, 803 (1926).

$$f_{oo} = 2a_o(8 + K^2a_o^2)/(4 + K^2a_o^2)^2 \tag{20}$$

where $K = 2k_o \sin(\theta/2)$ and $a_o = \hbar^2/me^2$ is the radius of the first Bohr orbit. Since $k_o = 2\pi mv/h$, the scattering amplitude is a function of the product of the velocity of the incident electron and the $\sin(\theta/2)$, where θ is the angle through which the scattering takes place.

The "exchange" scattering amplitude g_{oo} for the first Born approximation, obtained by substituting (19) into (18) via (17), is given by Massey and Mohr[5] as

$$g_{oo} = 4a_o \sum_{n=0}^{\infty} g_n P_n(\cos \theta) \tag{21}$$

where the g_n are functions of $k_o a_o$ and the $P_n(\cos \theta)$ are Legendre polynomials. The actual numerical calculations of g_{oo} were not carried out for the high energies of interest to us by Massey and Mohr. We have therefore calculated g_{oo} for an incident electron energy of 350 volts for values of $k_o a_o \sin(\theta/2)$ from 0 to 5, which corresponds to an angular range of $0°$ to $160°$. These values are compared with the corresponding f_{oo} values in Table 1. The table also contains the values of the elastic scattering cross sections [cf. Eq. (5)] with and without the contribution of "exchange" (i. e., g_{oo}) to the scattering. It is

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[5]H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A 132, 608 (1931).

TABLE 1

**ELASTIC SCATTERING COEFFICIENTS AND CROSS SECTIONS
CALCULATED BY BORN APPROXIMATION WITH AND WITHOUT
ALLOWANCE FOR EXCHANGE EFFECTS**

$k_o a_o \sin\theta/2$	f_{oo}/a_o	g_{oo}/a_o	$I(\theta) = |f_{oo}|^2$	$I(\theta) = $ $3/4 |f-g|^2 + 1/4 |f+g|^2$
0.00	1.0000	-0.0288	27.9	28.7
0.03	.999	-0.0288	27.9	28.7
0.05	.996	- .029	27.7	28.5
0.10	.985	- .029	27.1	27.7
0.20	.943	- .029	24.8	25.6
0.30	.880	- .028	21.6	22.3
0.40	.803	- .028	18.0	18.6
0.50	.720	- .027	14.5	15.0
0.60	.638	- .026	11.4	11.8
0.70	.561	- .025	8.78	9.18
0.80	.491	- .024	6.73	7.06
0.90	.429	- .023	5.14	5.41
1.0	.375	- .022	3.93	4.18
1.2	.289	- .019	2.33	2.49
1.4	.226	- .017	1.43	1.54
1.6	.180	- .014	0.904	0.979
1.8	.146	- .010	0.593	0.636
2.0	.120	- .007	0.402	0.427
2.5	.0773	- .0011	0.172	0.169
3.0	.0550	+0.0024	0.084	0.081
3.5	.0406	+ .0026	0.046	0.043
4.0	.0311	+ .0001	0.027	0.027
4.5	.0246	-0.0018	0.017	0.018
5.0	.0200	+0.0034	0.011	0.0092

apparent that the "exchange" effect can be neglected at such high energies and the cross section for elastic scattering of electrons by hydrogen atoms can then be written simply

$$I_{oo}(\theta \phi) = |f_{oo}|^2 . \qquad (22)$$

as follows from Eq. (5) with $g_{oo} = 0$.

The adequacy of the Born approximation is determined by a comparison of the elastic scattering cross sections calculated from (22) and (20) with observed scattered intensities. Such a comparison was made by Webb[6] in his report of the experimental determinations of cross sections for the elastic scattering by hydrogen[7] of electrons with incident energies varying from 30 to 912 volts over the angular range from 5° to 150°. In accordance with the assumption that the interaction of electron and atom is very small, the agreement between the Born approximation and experimental curves[8] is best at the

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[6] Glenn M. Webb, Phys. Rev. 47, 384 (1935).

[7] Molecular hydrogen was used. For the comparison of theoretical and experimental results, the cross sections calculated for atomic hydrogen by the Born formula were transformed by a suitable factor to equivalent cross sections for scattering by molecular hydrogen. See part IV A.

[8] The intensities of the scattered electrons at different angles are measured only relative to each other in scattering experiments. Hence the cross sections are reported in arbitrary units and the curves are compared with the corresponding theoretical curves by adjusting the ordinates of the experimental curves so as to obtain the best fit to the theoretical curves.

highest energy, 912 volts. At this energy, the experimental points lie on the calculated curve from 10° to 60°. The angular range of the agreement decreases with decreasing energy. The experimental curves rise much more rapidly at small angles than the theoretical curves do. At large angles the observed points lie consistently above the calculated curves. At the lower voltages (30-100 volts) there is scarcely any agreement. At 350 volts, the Born formula seems adequate from 40° to 60°; the departure of the experimental curve from the theoretical curve at the small angles is very pronounced; although the agreement is not good at the large angles, the deviations are small compared to those at the small angles. Thus, the scattering of 350 volt electrons can be taken as a good test case of the adequacy of any theoretical calculation which attempts to improve to some extent the Born approximation. It is for this reason that we adopted this particular energy for the work described in the following pages.

The second Born approximation involves the substitution of the expression (12) for $F_o(\vec{r}_2)$, obtained by the first Born approximation, as part of the function $\Psi(\vec{r}_1, \vec{r}_2)$ in Eq. (10) and the integrations of the equations a second time. This procedure is so involved that the calculation has never been carried through. It would be preferable to begin with a more accurate approximation of $\Psi(\vec{r}_1, \vec{r}_2)$ than to obtain successive Born approximations by iteration.

Another method, due to Massey and Mohr,[9] uses the second Born approximation only to obtain a "polarization" potential. With this potential added to the static potential of the atom, the cross sections are recalculated by the method of the first Born approximation. Although the method cannot be justified rigorously (in the mathematical sense), the agreement of the theoretical and observed cross section curves is considerably better than that afforded by the first Born approximation at small angles.[6]

There is still considerable room for improvement of the first Born approximation by some simple analytical means. In search of such a method we have investigated variational techniques.

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[9] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A 146, 880 (1934).

II. THE VARIATIONAL METHOD

A. Methods of Hulthèn and Kohn--The variational

procedures introduced by Hulthèn[10] and Kohn[11] treat the one-body problem consisting of the scattering of a particle by a potential $V(r)$. They involve the construction of an integral

$$L(\vec{k}_1, -\vec{k}_2) = \int \Psi_2 (E - H) \Psi_1 d\tau , \qquad (23)$$

where $(E - H) = \left[\nabla^2 + k^2 - V(r) \right]$. When Ψ is a proper solution of $H \Psi = E \Psi$, satisfying the boundary condition

$$\Psi_i \xrightarrow[r \to \infty]{} \exp(i\vec{k}_i \cdot \vec{r}) + f(\vec{k}_i, \vec{k}) \exp(ikr)/r \quad (i = 1, 2) , \qquad (24)$$

the integral (23) vanishes. In the event that an exact solution Ψ is not known, but a trial function $\Psi_t = \Psi + \delta \Psi$ can be set up, which has the same asymptotic form as Ψ of (24) but with f replaced by $f + \delta f$, then it can be shown that to first order,[11]

$$\delta L(\vec{k}_1, -\vec{k}_2) = -4\pi \, \delta f(\vec{k}_1, -\vec{k}_2). \qquad (25)$$

Hence a variational procedure is available for calculating the unknown

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[10]L. Hulthèn, Kungl. Fysio. Sällskapets Lund Förhand. 14, 1 (1944).

[11]W. Kohn, Phys. Rev. 74, 1763 (1948).

f. If a trial function is

$$\Psi_t = \Psi_t(\vec{r}, c_1, c_2, c_3, \ldots, f_t) \tag{26}$$

where the c_i and f_t are parameters, numerical values of these parameters may be obtained by solving the simultaneous equations derived from (25):

$$\left.\begin{array}{l} \partial L/\partial c_i = 0, \\[2mm] \partial L/\partial f = -4\pi \end{array}\right\} \text{according to Kohn's linear method} \qquad \begin{array}{l}(27a)\\[4mm](27b)\end{array}$$

or

$$\left.\begin{array}{l} L = 0, \\[2mm] \partial L/\partial c_i = 0 \end{array}\right\} \text{according to Hulthèn's quadratic} \qquad \begin{array}{l}(28a)\\[4mm](28b)\end{array}$$

method.

Kohn's method then gives

$$4\pi f = L_t + 4\pi f_t \tag{29}$$

while Hulthèn's method gives

$$f = f_t \tag{30}$$

because of the stipulation that $L = 0$. It is apparent that the better the trial function, the better the agreement between the scattering amplitude given by Kohn's method and that given by Hulthèn's method since in the limit of $\Psi_t \rightarrow \Psi$, $L_t \rightarrow 0$ and the two methods give the same results.

Variational techniques have been applied successfully to the elastic scattering of low energy ($<$ 13 volts) electrons by hydrogen atoms. Huang, [12] using a modified Hulthèn variational procedure, calculated the phase shifts for S-wave scattering. [13] He employed a trial function

$$\Psi(r_1, r_2) = \left[\exp(-r_1)/r_2\right]\left[\sin kr_2 + u(r_1 r_2)\cos kr_2\right], \quad (31)$$

$$u = \left[1 - \exp(-r_2)\right]\left[a + (b + cr_{12})\exp(-r_2)\right],$$

where a, b, and c are variational parameters. His results were inconclusive, however, due to a mistake in his method. [14]

Massey and Moiseiwitsch[15] applied the variational methods of Kohn and Hulthèn to the elastic scattering of slow electrons by H-atoms. They used Huang's trial function and combinations of it to allow for exchange in the determination of the S-wave phase shifts.

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[12] Su-Shu Huang, Phys. Rev. __76__, 477 (1949).

[13] The scattered wave can be considered as a sum of partial waves of phase η_n. (See, e.g., Mott and Massey, op. cit., Chap. II.) The S-wave scattering is that part of the scattering which is spherically symmetric (not dependent on the angle θ) and the total S-wave cross section is given by $Q = (4\pi/k^2)\sin^2 \eta_0$. S-wave scattering predominates at low energies.

[14] L. Hulthèn and P. O. Olsson, Phys. Rev. __79__, 531 (1950).

[15] H. S. W. Massey and H. L. Moiseiwitsch, Proc. Roy. Soc. __A 205__, 483 (1951).

The fact that both (Kohn and Hulthèn) variational methods gave very nearly the same results indicates that the trial function (31) is a fairly good approximation to the exact wave function for the scattering of slow electrons. In the absence of experimental data for e-H scattering at low energies, the scattering amplitudes were checked with the previous results obtained by direct numerical integrations of the differential equation -- the agreement was found excellent.

On the basis of the good results obtained for the elastic scattering of slow electrons, it should be possible to apply a variational technique to investigate the elastic scattering of fast electrons by hydrogen atoms. For this purpose the variational equations of Huang or Massey and Moiseiwitsch cannot be applied since they are formulated on the assumption that only S-wave scattering takes place.

B. Variational Procedure for Improving the Born Approximation for e-H Scattering--A solution of the wave equation (1) for the scattering of an electron by a hydrogen atom has the asymptotic form (cf. Eq. (2))

$$\Psi_o^{(1)} \rightarrow \psi_o(\vec{r}_1) \exp(ik_o \vec{n}^{(1)} \cdot \vec{r}_2)$$
$$+ (1/r_2) \sum_m \psi_m(\vec{r}_1) \quad f_{mo}(\vec{n}^{(1)}; \vec{n}_2) \exp(ik_m r_2) , \quad (32a)$$
$$\text{as } r_2 \rightarrow \infty;$$

$$\Psi^{(1)}_o \rightarrow (1/r_1) \sum_m \psi_m(\vec{r}_2) g_{mo}(\vec{n}^{(1)};\vec{n}_1) \exp(ik_m r_1), \tag{32b}$$

$$\text{as } r_1 \rightarrow \infty.$$

In order to derive a variational equation for calculating f_{oo} specifically another solution to the same wave equation with the asymptotic form

$$\Psi^{(2)}_{o*} \rightarrow \psi^*_o(\vec{r}_1) \exp(-ik_o \vec{n}^{(2)} \cdot \vec{r}_2)$$

$$+ (1/r_2) \sum_m \psi^*_m(\vec{r}_1) f_{mo*}(\vec{n}^{(2)};\vec{n}_2) \exp(ik_m r_2), \tag{33a}$$

$$\text{as } r_2 \rightarrow \infty;$$

$$\rightarrow (1/r_1) \sum_m \psi^*_m(\vec{r}_2) g_{mo*}(\vec{n}^{(2)};\vec{n}_1) \exp(ik_m r_1), \tag{33b}$$

$$\text{as } r_1 \rightarrow \infty;$$

is introduced. The integral [cf. (23)]

$$L_{oo}(\vec{n}^{(1)};\vec{n}^{(2)}) = \int \Psi^{(2)}_{o*}(E - H) \Psi^{(1)}_o \, d\tau_1 d\tau_2, \tag{34}$$

where $H = (-\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) - (e^2/r_1) - (e^2/r_2) + (e^2/r_{12})$,

is constructed and its first-order variation is obtained by replacing each Ψ by $\Psi + \delta\Psi$, where the $\Psi + \delta\Psi$ have the same asymptotic form as Ψ, but with each f and g replaced by $f + \delta f$ and $g + \delta g$. Making use of Green's theorem, we then have

$$\delta L_{oo} = E_o a_o^2 \int_{r_1 \to \infty} \left[\Psi_{o*}^{(2)} \nabla_1 \delta \Psi_o^{(1)} - \delta \Psi_o^{(1)} \nabla_1 \Psi_{o*}^{(2)} \right] \cdot d\sigma_1 d\tau_2$$

$$+ E_o a_o^2 \int_{r_2 \to \infty} \left[\Psi_{o*}^{(2)} \nabla_2 \delta \Psi_o^{(1)} - \delta \Psi_o^{(1)} \nabla_2 \Psi_{o*}^{(2)} \right] \cdot d\sigma_2 d\tau_1. \quad (35)$$

Substituting into (35) the asymptotic forms (33) and the variation
of (32), and performing the volume integrations, we find that the
first of these integrals vanishes so that (35) then reduces to

$$\delta L_{oo} = E_o a_o^2 \int_{r_2 \to \infty} \exp(-ik_o r_2 \cos \alpha) \, \delta f_{oo}(\vec{n}^{(1)}; \vec{n}_2) \exp(ik_o r_2)/r_2 \times$$

$$\left[ik_o \cos \alpha + ik_o \right] r_2^2 \, 2\pi \sin \alpha \, d\alpha, \quad (36)$$

where $\cos \alpha = \vec{n}^{(2)} \cdot \vec{n}_2$. An integration by parts then gives
$\left[\text{cf. (25)} \right]$.

$$\delta L_{oo}(\vec{n}^{(1)}; \vec{n}^{(2)}) = -4\pi E_o a_o^2 \, \delta f_{oo}(\vec{n}^{(1)}; \vec{n}^{(2)}). \quad (37)$$

Eq. (37) provides a variational equation for calculating f_{oo}. A similar
equation is obtained for g_{oo} if the roles of $\vec{r}_1$ and $\vec{r}_2$ are interchanged
in $\Psi_{o*}^{(2)}$.

We try out this variational equation with the simple trial
functions (the one used for the Born approximation -- cf. Eq. (19)):

$$\Psi_t^{(1)}(\vec{r}_1, \vec{r}_2) = \psi_o(\vec{r}_1) \exp(ik_o \vec{n}^{(1)} \cdot \vec{r}_2), \quad (38a)$$

and $\Psi_t^{(2)}(\vec{r}_1, \vec{r}_2) = \Psi_o^*(\vec{r}_1) \exp(-ik_o\vec{n}^{(2)} \cdot \vec{r}_2)$. (38b)

Then since we have $f_t = 0$, it follows from (37) that

$$f_{oo}(\vec{n}^{(1)}; \vec{n}^{(2)}) = 1/(4\pi E_o a_o^2) L_t(\vec{n}^{(1)}; \vec{n}^{(2)}) . \quad (39)$$

Substituting (38a), (38b) into (34), we find

$$L_t = 8\pi E_o a_o^3 (8 + K^2 a_o^2)/(4 + K^2 a_o^2)^2 \quad (40)$$

Substituting (40) into (39), we obtain

$$f_{oo}(\theta) = 2a_o(8 + K^2 a_o^2)/(4 + K^2 a^2)^2 , \quad (41)$$

which is exactly the scattering amplitude (20) obtained for the first
Born approximation. Hence, it appears that Eq. (37) provides a
variational method for improving the Born approximation.

C. Selection of Trial Function--The scattering process we
are considering may be broken down into the following components:[9]

1. Scattering by the field of the atom, considering the
   atom undisturbed by the incident electron and the incident
   electron only slightly affected by the collision;

2. The distortion of the incident and scattered electron
   waves by the potential field of the atom (the latter
   field being taken as the undisturbed atomic field);

3. The disturbance or "polarization" of the atomic field by the incident and scattered electron waves;

4. The exchange of electrons between the incident electron wave and the atom.

The trial function adopted should allow for as many of these component processes as possible. The number of parameters in our trial function was limited to three in order that the calculations should not become unduly cumbersome. (Massey and Moiseiwitsch[15] found three parameters sufficient to give excellent results--see above.) Adapting Huang's trial function (31), which gave such good results at low energies, for use at high energies, we obtain a trial function

$$\Psi_t = \psi_o(\vec{r}_1)\exp(i k_o \vec{n} \cdot \vec{r}_2)\left[1 + b\exp(-r_2/a_o) + (c r_{12}/a_o) \times \exp(-r_2/a_o)\right] + A\left[\exp(i k_o r_2)/r_2\right]\left[1 - \exp(-r_2/a_o)\right]\psi_o(\vec{r}_1). \quad (42)$$

The first term in the bracket gives the Born approximation and therefore allows for the first process in the list above. The second term allows for effects on the incident wave close to the hydrogen atom since $\exp(-r_2/a_o)$ falls off rapidly for values of r_2 greater than a_o, the radius of the first Bohr orbit; this term attempts to take care of the distortion of the incident wave by the field of the atom listed as part of process 2. The third term $(c r_{12}/a_o)\exp(-r_2/a_o)$ allows for the polarization of the atomic field by its explicit dependence on the

the distance between the incident and atomic electrons. This term will have a peak value in the vicinity of the atom but will also be zero when the two electrons' positions coincide; it attempts to take care of process 3. The effect of an exchange of the incident and atomic electrons on the scattered electron wave (process 4) has been discussed in the Introduction (p. 8). At the energy considered (350 volts), the effect of exchange is not significant (see Table 1). In the last term, A is the trial scattering coefficient. The factor $\left[1 - \exp(-r_2/a_o) \right]$ is included so that the wave function behaves properly when r_2 approaches zero, and this factor is appreciably different from unity only in the neighborhood of the atom. A very important reason for choosing the trial function in the particular form of (42) is to make the required integrations involving the function feasible (see III A). The asymptotic form of (42) is

$$\Psi_t \underset{r_2 \to \infty}{\longrightarrow} \Psi_o(\vec{r}_1) \left[\exp(ik_o\vec{n}\cdot\vec{r}_2) + A \exp(ik_o r_2)/r_2 \right] . \tag{43}$$

III. THE CALCULATIONS

A. The Variational Integral L_{oo}--To obtain the scattering coefficient f_{oo} for the elastic scattering of electrons by hydrogen atoms in the ground state, the integrations involved in L_{oo} of (34) must be carried out. In addition to the trial function

$$\Psi_t^{(1)} = \psi_o(\vec{r}_1)\exp(ik_o\vec{n}^{(1)}\cdot\vec{r}_2)\left[1 + b\exp(-r_2/a_o)\right.$$
$$+ (cr_{12}/a_o)\exp(-r_2/a_o)\right] + A\left[\exp(ik_o r_2)/r_2\right]\left[1\right.$$
$$\left. - \exp(-r_2/a_o)\right]\psi_o(\vec{r}_1) \quad (44)$$

selected above $\left[\text{cf. (42)}\right]$, an auxiliary trial function $\left[\text{cf. (33)}\right]$

$$\Psi_t^{(2)} = \psi_o^*(\vec{r}_1)\exp(-ik_o\vec{n}^{(2)}\cdot\vec{r}_2)\left[1 + b\exp(-r_2/a_o)\right.$$
$$+ (cr_{12}/a_o)\exp(-r_2/a_o)\right] + A\left[\exp(ik_o r_2)/r_2\right]\left[1\right.$$
$$\left. - \exp(-r_2/a_o)\right]\psi_o^*(\vec{r}_1) \quad (45)$$

is required. Then

$$L_{oo} = \int \Psi_t^{(2)}(\vec{r}_1, \vec{r}_2)\left[E - H\right]\Psi_t^{(1)}(\vec{r}_1, \vec{r}_2)d\tau_1 d\tau_2$$
$$= 4\pi E_o a_o^2 (D_o + D_1 b + D_2 b^2 + D_3 c + D_4 c^2$$
$$+ D_5 A + D_6 A^2 + D_7 bc + D_8 bA + D_9 cA) \quad (46)$$

22

where, with $K = 2k_o \sin \theta/2$,

$$D_o = 2a_o(8 + K^2 a_o^2)/(4 + K^2 a_o^2)^2$$

$$D_1 = 4a_o\left[-K^2 a_o^2/(1 + K^2 a_o^2)^2 + (15 + K^2 a_o^2)/(9 + K^2 a_o^2)^2\right]$$

$$D_2 = 2a_o\left[-2(1 + K^2 a_o^2)/(4 + K^2 a_o^2)^2\right.$$
$$\left. + (24 + K^2 a_o^2)/(16 + K^2 a_o^2)^2\right]$$

$$D_3 = 4a_o(K^2 a_o^2 - 1)/(1 + K^2 a_o^2)^2$$
$$+ a_o(-132 - 10K^2 a_o^2)/(9 + K^2 a_o^2)^2 + (3/K)\left[-\tan^{-1}(1/Ka_o)\right.$$
$$\left. - \tan^{-1}(3/Ka_o)\right]$$

$$D_4 = 2a_o(64 - 104K^2 a_o^2 - 6K^4 a_o^4 - 3K^6 a_o^6)/(4 + K^2 a_o^2)^4$$
$$- 4a_o/(4 + K^2 a_o^2)^2$$

$$D_5 = -1 + (1 + k_o^2 a_o^2)^{-1} - 4(9 + 4k_o^2 a_o^2)^{-1}$$
$$+ (2/k_o a_o)\left[-\tan^{-1}(1/k_o a_o) + \tan^{-1}(3/2k_o a_o)\right] - i\left[k_o a_o\left\{(1\right.\right.$$
$$+ k_o^2 a_o^2)^{-1} - 8(27 + 12k_o^2 a_o^2)^{-1}\right\} + (1/k_o a_o)\left\{\ln(9 + 9k_o^2 a_o^2)\right.$$
$$\left.\left. - \ln(9 + 4k_o^2 a_o^2)\right\}\right]$$

$$D_6 = (1/a_0)\left[(2 + 2k_0^2a_0^2)^{-1} - 12(9 + 4k_0^2a_0^2)^{-1} + 2(4 + k_0^2a_0^2)^{-1}\right.$$

$$\left. - \ln(4 + 4k_0^2a_0^2) + 21\ln(9 + 4k_0^2a_0^2) - \ln(16 + 4k_0^2a_0^2)\right]$$

$$+ i\left[k_0\left\{(2 + 2k_0^2a_0^2)^{-1} - 8(9 + 4k_0^2a_0^2)^{-1} + (4 + k_0^2a_0^2)^{-1}\right\}\right.$$

$$\left. + (2/a_0)\left\{-\tan^{-1}(1/k_0a_0) + 2\tan^{-1}(3/2k_0a_0) - \tan^{-1}(2/k_0a_0)\right\}\right]$$

$$D_7 = 2a_0(-2-K^2a_0^2)/(4 + K^2a_0^2)^2 + 4a_0(-64-3K^2a_0^2)/(16 + K^2a_0^2)^2$$

$$+ (4/K)\left[-\tan^{-1}(2/Ka_0) + \tan^{-1}(4/Ka_0)\right]$$

$$D_8 = -1 + (2 + 2k_0^2a_0^2)^{-1} + 4(9 + 4k_0^2a_0^2)^{-1} - (4 + k_0^2a_0^2)^{-1}$$

$$+ (2/k_0a_0)\left[-\tan^{-1}(3/2k_0a_0) + \tan^{-1}(2/k_0a_0)\right]$$

$$+ i\left[k_0a_0\left\{(2 + 2k_0^2a_0^2)^{-1} + 8(27 + 12k_0^2a_0^2)^{-1} - (8 + 2k_0^2a_0^2)^{-1}\right\}\right.$$

$$\left. + (1/k_0a_0)\left\{\ln(36 + 16k_0^2a_0^2) - \ln(36 + 9k_0^2a_0^2)\right\}\right]$$

$$D_9 = -9(1 + 4k_0^2a_0^2)^{-1} - (4k_0^2a_0^2 + 9)^{-1} + (5 - 2k_0^2a_0^2)/(4 + 4k_0^2a_0^2)$$

$$- 11/12 + (1/2)\ln(81 + 36k_0^2a_0^2) - (1/2)\ln(16 + 64k_0^2a_0^2)$$

$$- (1/k_0a_0)\left[(5/2)\tan^{-1}(1/2k_0a_0) + 3\tan^{-1}(1/k_0a_0)\right.$$

$$\left. + (1/2)\tan^{-1}(3/2k_0a_0)\right] + i\left[k_0a_0\left\{-19(1 + 4k_0^2a_0^2)^{-1}\right.\right.$$

$$\left.\left. + 7(4 + 4k_0^2a_0^2)^{-1} - 2(27 + 12k_0^2a_0^2)^{-1}\right\} + (1/k_0a_0)\right.\quad x$$

$$\left\{(5/4)\ln(1 + 4k_o^2 a_o^2) + (3/2)\ln(1 + k_o^2 a_o^2)\right.$$

$$+ (1/4)\ln(9 + 4k_o^2 a_o^2) - (1/2)\ln 3\right\} + \tan^{-1}(3/2k_o a_o)$$

$$\left. - \tan^{-1}(1/2k_o a_o)\right].$$

The coefficient D_o is the same as the Born approximation scattering
amplitude of Eq. (20). Some of the coefficients D_i depend only on
the kinetic energy of the incident electron (i.e., k_o), while other
coefficients depend both on the kinetic energy of the incident electron
and the scattering angle Θ (i.e., K).

B. Linear Determination of Parameters--If the variational
method of Kohn is paralleled [cf. (27)], we have from Eq. (37) and
Eq. (46) the following set of linear equations

$$\partial L / \partial b = D_1 + 2D_2 b + D_7 c + D_8 A = 0 \qquad (47a)$$

$$\partial L / \partial c = D_3 + D_7 b + 2D_4 c + D_9 A = 0 \qquad (47b)$$

$$(4\pi E_o a_o^2)^{-1} \partial L / \partial A = D_5 + D_8 b + D_9 c + 2D_6 A = -1 \qquad (47c)$$

for determining b, c, and A. Whence,

$$L_{oo}(b, c, A) = -4\pi E_o a_o^2 (A - f_{oo}) \qquad (48a)$$

determines f_{oo}:

$$f_{oo} = D_o + A + D_5 A + D_6 A^2 + D_1 b + D_2 b^2 + D_3 c$$

$$+ D_4 c^2 + D_7 bc + D_8 bA + D_9 cA . \tag{48b}$$

Numerical values of the coefficients D_i have been calculated for electrons of 350 volt energy over a range of θ from $0°$ to $160°$. Using these numerical values, Eqs. (47) were solved simultaneously for the parameters b, c, and A. The values of these parameters are listed in Table 2. Numerical values of f_{oo} and the cross sections

$$I_{oo}(\theta) = |f_{oo}(\theta)|^2 \tag{49}$$

were then obtained via (48b). These values are tabulated along with the cross sections given by Born's formula (i. e., Eq. (20)) in Table 3. A comparison is made graphically in Figure 1.

It is seen from Eq. (48b) that the linear variational method gives the scattering coefficient as the sum of the Born approximation scattering coefficient (i. e., D_o) and additional contributions from the trial scattering amplitude (A) and from the parameters (b, c) which were chosen to allow for the effects of distortion and polarization. Figure 1 shows that allowance for these additional contributions to the scattering amplitude results in a sharp rise in the cross section curve at small angles well beyond the Born approximation

TABLE 2

PARAMETERS DETERMINED BY LINEAR METHOD
FOR 350 VOLT ELECTRONS

$k_o a_o \sin \theta/2$	b	c	A/a_o
0	$-8.56 + 8.69i$	$4.31 - 1.23i$	$0.921 - 0.596i$
0.03	$-8.42 + 8.38i$	$4.21 - 1.15i$	$.892 - .585i$
.05	$-8.33 + 8.75i$	$4.25 - 1.29i$	$.900 - .621i$
.1	$-7.52 + 8.17i$	$4.02 - 1.29i$	$.771 - .678i$
.2	$-4.78 + 7.06i$	$2.77 - 1.38i$	$.464 - .724i$
.3	$-0.358 + 4.24i$	$0.812 - 1.24i$	$-0.0874 - .601i$
.4	$-1.22 + .109i$	$.358 + 0.261i$	$-.0432 - .115i$
.5	$-2.25 - 0.524i$	$.587 + .648i$	$0.139 - .00326i$
.6	$-2.40 - .649i$	$.618 + .712i$	$.244 + 0.0376i$
.7	$-2.05 - .454i$	$.540 + .584i$	$.218 + .0302i$
.8	$-1.78 - .437i$	$.454 + .529i$	$.209 + .0422i$
.9	$-1.56 - .442i$	$.382 + .490i$	$.194 + .0521i$
1.0	$-1.32 - .421i$	$.308 + .441i$	$.168 + .0525i$
1.2	$-0.965 - .363i$	$.203 + .360i$	$.122 + .0444i$
1.4	$-.750 - .381i$	$.129 + .328i$	$.0914 + .0416i$
1.6	$-.580 - .360i$	$.0768 + .291i$	$.0673 + .0330i$
1.8	$-.455 - .340i$	$.0397 + .262i$	$.0502 + .0257i$
2.0	$-.360 - .328i$	$.0103 + .242i$	$.0383 + .0205i$
2.5	$-.203 - .291i$	$-0.0344 + .202i$	$.0209 + .0115i$
3.0	$-.109 - .272i$	$-.0621 + .178i$	$.0128 + .00720i$
3.5	$-.0410 - .258i$	$-.0819 + .161i$	$.00819 + .00498i$
4.0	$-.0156 - .237i$	$-.0856 + .152i$	$.00578 + .00314i$
4.5	$+0.0186 - .230i$	$-.0932 + .143i$	$.00435 + .00255i$
5.0	$+.0439 - .219i$	$-.105 + .132i$	$.00344 + .00202i$

TABLE 3

ELASTIC SCATTERING COEFFICIENTS AND CROSS SECTIONS DETERMINED BY LINEAR VARIATIONAL METHOD COMPARED TO BORN APPROXIMATION

$k_o a_o \sin \theta/2$	f_{oo}/a_o	$I(\theta)$ Linear Var. Method	$I(\theta)$ Born Approximation
0	$-9.91 + 5.54i$	$3595 \times 10^{-18} cm^2$	$27.9 \times 10^{-18} cm^2$
0.03	$-9.54 + 5.20i$	3295	27.9
.05	$-9.31 + 5.42i$	3239	27.7
.1	$-7.65 + 4.56i$	2213	27.1
.2	$-2.64 + 2.44i$	362	24.8
.3	$0.456 + 0.583i$	15.3	21.6
.4	$.900 - 0.0838i$	22.8	18.0
.5	$1.12 + 0.100i$	35.3	14.5
.6	$1.36 + .212i$	37.2	11.4
.7	$0.975 + .181i$	27.4	8.78
.8	$.808 + .163i$	19.0	6.73
.9	$.663 + .143i$	12.8	5.14
1.0	$.535 + .113i$	8.34	3.93
1.2	$.363 + .0494i$	3.75	2.33
1.4	$.261 + .0454i$	1.95	1.43
1.6	$.196 + .0292i$	1.09	0.904
1.8	$.153 + .0191i$	0.661	.593
2.0	$.123 + .0131i$	.425	.402
2.5	$.0771 + .00565i$	.167	.172
3.0	$.0544 + .00292i$	.0829	.084
3.5	$.0400 + .00167i$	.0448	.046
4.0	$.0308 + .00104i$	.0265	.027
4.5	$.0244 + .00074i$	.0166	.017

Fig. 1. The theoretical cross sections, obtained by the linear (Kohn) and quadratic (Hulthèn) variational procedures, for the elastic scattering of 350 volt electrons by hydrogen atoms are compared to the cross sections calculated by the Born approximation and to the relative scattered intensities measured by Webb. Ordinate, Elastic scattering cross sections in units of 10^{-18} cm^2 Abscissa, Angle Θ through which the scattering takes place.

Linear var. method — Quadratic var. method — Born approx. ∘ Experimental values
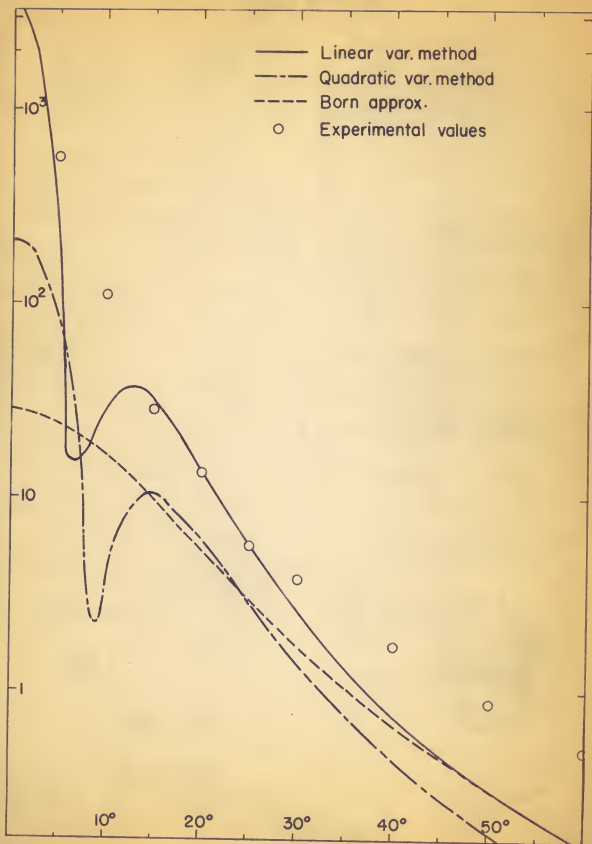
curve. At large angles, however, the two curves merge.

C. Quadratic Determination of Parameters--If the varia-
tional method of Hulthèn is paralleled [cf. (28)], the restriction that
the trial function be such that the variational integral L vanishes is
imposed. Then, from (37),

$$\delta L_{oo} = -4 \pi E_o a_o^2 \delta f_{oo} = 0 \tag{50}$$

and

$$L_{oo} = 0 \tag{51a}$$

$$\partial L / \partial b = 0 \tag{51b}$$

$$\partial L / \partial c = 0 \tag{51c}$$

are the equations for determining b, c, and A. Note that (51b) and
(51c) are the same as (47a) and (47b) and hence linear in the parameters,
but that (51a) sets the expression for L_{oo} given by (46) equal to zero
and is therefore quadratic in the parameters while its counterpart in
the Kohn method, (47c), is linear. Eq. (50) also gives

$$f_{oo} = A , \tag{52}$$

as opposed to the expression (48b) for f_{oo} given by the linear (Kohn)
method.

The values of the parameters b and c were found in terms of

the parameter A by a simultaneous solution of Eqs. (51b) and (51c). Substituting these values into Eq. (51a), we obtained an equation of the second degree in A. Using the calculated values of D_i (see above), the two possible values of A were then calculated from this equation over the angular range considered--these two sets of values being equivalent to two sets of f_{oo} values via (52). A method for discriminating between these two sets of f_{oo} values was necessary and a test similar to that used by Massey and Moiseiwitsch[15] was employed.

Eq. (13) is an exact integral equation for the scattering coefficient f_{oo}. The integral of Eq. (13) was evaluated using the Ψ of (44) corresponding to each of the two sets of parameters resulting from the quadratic equation in A. The set of parameters for which the integral was more nearly equal to the value of A (= f_{oo}) tested was then the set of parameters selected.

The selected set of parameters b, c, and A calculated for 350 volt electrons by the quadratic variational method is given in Table 4. The corresponding values of the integral in (13) are also listed for comparison with the values of the scattering coefficient A. It is apparent from the table that the agreement between the integral equation values of f_{oo} and the values of A is not very good except at large angles. But it is still sufficiently good to discriminate between the two sets of f_{oo} values. The cross sections calculated by this method are compared to those calculated by the Born approximation

TABLE 4

PARAMETERS DETERMINED BY QUADRATIC METHOD FOR 350 VOLT ELECTRONS

$k_0 a_0 \sin\theta/2$ (ρ)	b	c	A/a_0	Integral/a_0
0.05	-21.6 +16.9i	4.26 -3.56i	2.66 -0.634i	-11.1 +10.1i
.1	-20.9 +17.1i	4.23 -3.70i	2.62 -.668i	-10.6 +10.1i
.2	-18.7 +16.9i	4.01 -3.87i	2.43 -.788i	-9.04 +9.60i
.3	-10.6 +14.7i	2.66 -4.02i	1.59 -1.01i	-3.77 +7.02i
.4	+2.43 +10.0i	-1.65 -4.00i	0.111 -1.04i	0.178 +3.34i
.5	-1.83 -2.92i	0.278 +3.65i	.172 -0.229i	.309 +0.282i
.6	-3.07 -1.66i	.499 +2.62i	.463 -.179i	.0171 +.825i
.7	-3.16 -1.50i	.454 +2.34i	.580 -.134i	-.0348 +.914i
.8	-2.70 -0.937i	.365 +1.88i	.552 -.130i	.0251 +.841i
.9	-2.31 -.865i	.268 +1.64i	.502 -.0892i	.0430 +.692i
1.0	-1.99 -.859i	.190 +1.47i	.444 -.0518i	.0505 +.553i
1.2	-1.68 -.825i	.129 +1.32i	.376 -.0312i	.0657 +.435i
1.4	-1.23 -.724i	.0524 +1.109i	.270 -.0143i	.0797 +.278i
1.6	-0.962 -.793i	.0114 +0.994i	.199 -.00131i	.0782 +.181i
1.8	-.773 -.789i	-.0152 +.917i	.150 -.00082i	.0739 +.125i
2.0	-.644 -.792i	.0322 +.868i	.117 -.00214i	.0671 +.0899i
2.5	-.548 -.816i	.0524 +.845i	.0942 -.00259i	.0592 +.0667i
3.0	-.392 -.840i	.0826 +.795i	.0588 -.00329i	.0426 +.0353i
3.5	-.312 -.893i	.0996 +.790i	.0409 -.00322i	.0326 +.0212i
4.0	-.251 -.972i	.116 +.809i	.0298 -.00254i	.0252 +.0135i
4.5	-.241 -.968i	.109 +.793i	.0229 -.00284i	.0198 +.00966i
5.0	-.174 -.952i	.137 +.756i	.0174 -.00142i	.0161 +.00654i
	-.175 -.889i	.114 +.716i	.0140 -.00160i	.0137 +.00527i

in Table 5 and graphically in Figure 1. It is evident that the quadratic (Hulthèn) method does not provide any significant change in cross section values from those of the Born approximation.

It should be noted that Eq. (13) is a necessary, but not sufficient, condition for the trial wave function to be a good approximation to the true wave function and that the linear (Kohn) variational procedure is such that this integral equation is satisfied identically. On the other hand, it should be noted that $L_{oo} = 0$ is also a necessary, but not sufficient, condition for the trial wave function to be a good approximation to the true wave function and that the quadratic (Hulthèn) method is such that this condition is satisfied identically.

TABLE 5

CROSS SECTIONS DETERMINED BY QUADRATIC VARIATIONAL
METHOD COMPARED TO
BORN APPROXIMATION---350 VOLT ELECTRONS

$k_o a_o \sin \theta/2$	θ		$I(\theta)$	
			Quad. Var. Method	Born Approx.
0	0°	$0'$	$209 \times 10^{-18} cm^2$	$27.9 \times 10^{-18} cm^2$
0.05	1	8	204	27.7
.1	2	16	182	27.1
.2	4	32	99.1	24.8
.3	6	44	30.5	21.6
.4	9	0	2.29	18.0
.5	11	18	6.87	14.5
.6	13	34	9.89	11.4
.7	15	58	8.97	8.78
.8	18	4	7.27	6.73
.9	20	28	5.58	5.14
1.0	22	46	3.97	3.93
1.2	27	22	2.04	2.33
1.4	32	4	1.10	1.43
1.6	36	48	0.629	0.904
1.8	41	36	.381	.593
2.0	46	28	.248	.402
2.5	59	6	.0968	.172
3.0	72	34	.0469	.084
3.5	87	18	.0249	.046
4.0	104	10	.0149	.027
4.5	125	8	.00851	.017
5.0	160	56	.00550	.011

IV. COMPARISON OF THEORETICAL CALCULATIONS
WITH EXPERIMENTAL DATA

A. Adjustment of Experimental Data for Scattering by
Atomic Hydrogen--The bulk of the experimental data for electron-
hydrogen scattering has been taken for molecular hydrogen.[16]
Harnwell,[17] however, carried out investigations of the scattering of
electrons by both atomic and molecular hydrogen and reported that
the scattered intensities when atomic hydrogen is present are not
much different than when molecular hydrogen alone is present. Since
a difference is detectable, some allowance was made for it in the
comparison of our theoretical calculations and the experimental data.

Assuming the validity of the Born approximation, Massey
and Mohr[18] have obtained the ratio of the scattering by molecular
hydrogen to the scattering by atomic hydrogen:

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[16]The work of Webb[6] is so comprehensive that his results
alone are sufficient to test the adequacy of the theoretical values of
scattering cross sections. Webb measured the scattered intensity
over a wide range of angles and voltages with a single apparatus and
found, moreover, that his results agreed closely with those obtained
by other investigators in the overlapping regions.

[17]G. P. Harnwell, Phys. Rev. **34**, 661 (1929).

[18]H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc.
A 135, 258 (1932).

$$I_{H_2}/I_H = (1 + \sin x/x)\phi(y), \tag{53}$$

where $x = 2k_o d \sin (\theta/2)$, d being the equilibrium nuclear separation of the molecule, and $y = k_o a_o \sin(\theta/2)$. This ratio performs a damped oscillation about unity as a function of $(v)\sin(\theta/2)$. For an energy of 350 volts over the range of Webb's experimental points, its maximum value is 1.4 at $\theta = 5°$ and its minimum value is 0.78 at $\theta = 30°$. This relationship was used to convert Webb's experimental data at 350 volts for molecular hydrogen to equivalent data for atomic hydrogen.[6]

B. Comparison of Calculated Scattering Intensities with Experimental Data--The experimental values of the cross sections are given in arbitrary units. Hence, for a comparison to the results of this investigation, the adjusted experimental data (cf. section A above) were fitted to coincide at 25° with the theoretical values obtained by the linear (Kohn) variational procedure as shown in Figure 1. In addition to these curves, the results from the Born formula are also given in Figure 1.

An examination of this figure reveals that at small angles ($\theta < 30°$), where the deviation of the Born approximation curve from the experimental points is very large, the curve obtained by the linear variational method fits the experimental curve very well except near 7°. The dip in the theoretical curve at around 7° is probably not

significant. At less than 7°, we found that the contributions to the
scattering amplitude [cf. (48b)] of the terms which are functions of
the parameters b and c were very large and negative compared to the
scattering amplitude of the Born approximation. (The part of the
scattering amplitude due to the terms which are functions of the
parameter A was negligibly small over the entire range of θ.)
At angles greater than 7°, the Born term was largest; at angles
greater than 46°, terms other than the Born term were negligibly
small. The dip in the theoretical curve appears at about 7° where
the terms in b and c had become negative but were not yet larger than
the Born term. Hence the dip appears in a transition region between
the very small angular region where the (b and c) terms allowing for
polarization and distortion effects contributed most to the scattering
and the angular region ($\theta > 12^\circ$) where the Born term predominated.
It seems that three parameters are too few to make the transition
smoothly.

The cross section values obtained from the quadratic
(Hulthèn) variational procedure do not provide any improvement of
the Born approximation. In Figure 1, the curve obtained by the quad-
ratic method lies below the Born curve at the larger angles where
the experimental points lie higher than the Born curve while, at small
angles, it rises somewhat above the Born curve but not to such an
extent that it can be considered to agree better with the experimental

curve.

It is interesting to note that the shapes of the curves in
Figure 1 obtained by the two variational procedures are quite similar
even to the dip appearing around 7°, but that the curves are dis-
placed relative to one another. It follows from Eqs. (48a) and (52)
that the closer the trial function is to the exact wave function, the
closer the two cross section curves will agree. Hence, the displace-
ment of the two curves demonstrates that the trial wave function is
not a very good approximation to the exact wave function. The fact
that the trial wave function is not a good approximation to the true
wave function, however, does not necessarily mean the calculated
coefficients are not good approximations to the true scattering coef-
ficients. It is a peculiarity of quantum mechanical variational proce-
dures that satisfactory results can be obtained even though the simple
trial functions employed are relatively poor approximations.[19] This
is not surprising, however, since in our case, for example, the
theory provides a stationary expression for the scattering coefficient,
not the wave function. The criterion for adequacy of the theoretical
scattering cross sections is still "goodness of fit" to the experimental

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[19] For example, excellent results for the calculation of the
binding energy of the hydrogen molecule by a variational method
employing a very simple trial function were obtained by: W. Heitler
and F. London, Zeits. f. Physik. 44, 455 (1927).

data and the above results of our linear variational procedure do
provide a reasonably good fit.

C. Results Obtained by Linear Variational Procedure with
Various Other Trial Functions--The trial wave functions other than
Eq. (44) which we have used to determine the elastic scattering cross
section by the linear variational procedure are also worth consider-
ation. Especially interesting are the results we obtained with the trial
functions.

$$\Psi_t^{(1)} = \psi_0(\vec{r}_1) \exp(ik_0\vec{a}^{(1)}\cdot\vec{r}_2) \left[1 + b\exp(-r_2/a_0) + (cr_{12}/a_0)\exp(-r_2/a_0) \right] \qquad (54)$$

and

$$\Psi_t^{(2)} = \psi_0'(\vec{r}_1) \exp(-ik_0\vec{a}^{(2)}\cdot\vec{r}_2) \left[1 + b\exp(-r_2/a_0) + (cr_{12}/a_0)\exp(-r_2/a_0) \right], \qquad (55)$$

which are the same as (44) and (45) with $A = 0$. For this case,

$$f_{oo} = D_o + (D_1^2 D_4 + D_3^2 D_2 - D_1 D_3 D_7)/(D_7^2 - 4D_4 D_2). \qquad (56)$$

Reference to Eq. (46) shows that the D_i appearing in (56) are all
function of $Ka_0 = 2k_0 a_0 \sin(\theta/2)$. Therefore the scattering ampli-
tudes for the b and c parameter case (56), like those obtained by the

Born approximation (20), are functions of $(v)\sin(\theta/2)$ only.

In Figure 2, the results for the b, c parameter trial functions (54, (55) are compared to those previously derived for the A, b, c parameter trial functions (44), (45). The curves are very similar. It seems then that the good fit obtained with the linear method and trial functions (44), (45) to the experimental data, as shown in Figure 1, at the small angles is provided predominantly by the contributions of parameters b and c to the scattering amplitude. For the b, c parameter case, the parameter A is zero, and the quadratic variational procedure gives a zero scattering coefficient. From these considerations, it is understandable that the linear variational method has yielded better results than the quadratic variational method for the trial functions (44), (45) as discussed above.

The linear variational procedure using the trial functions considered so far provides no improvement of the Born approximation at large angles. At large angles, the experimental curve of the scattering cross section becomes almost independent of angle instead of falling off uniformly with increase of angle as predicted by the Born approximation. In Eq. (46) the coefficients D_i of the terms involving the parameter A are independent of angle. From this, it seems that parameters in the scattered wave part of the trial function may allow for the improvement of the theoretical curves at large angles. Considering a trial wave function of the general form

Fig. 2. The theoretical cross sections for the elastic scattering of 350 volt electrons by hydrogen atoms calculated by the linear (Kohn) variational procedure employing the trial functions (44), (45) with the parameter b (A, c = 0), with the parameter c (A, b = 0), and with parameters b, c (A = 0) are compared to those obtained using the parameters A, b, c in the same trial function. Ordinate, Elastic scattering cross sections in units of 10^{-18}cm.^{2} Abscissa, Angle Θ through which the scattering takes place.

Legend:
— A,b,c
–– b
–·– b,c
-- c
○ Experimental values
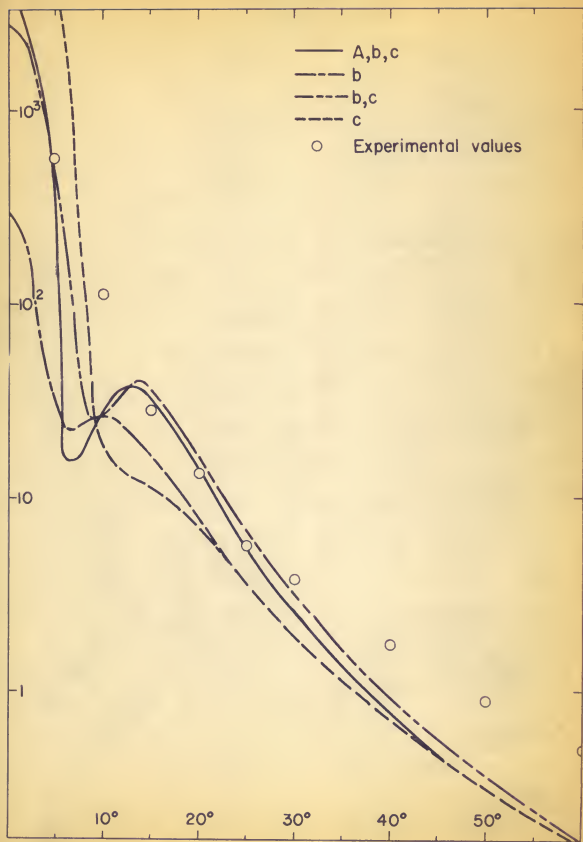
$$\Psi_t = \Psi_0(\vec{r}_1) \left[\exp(ik_0\vec{n}\cdot\vec{r}_2) \left\{ 1 + b\exp(-r_2/a_0) + (cr_{12}/a_0)\exp(-r_2/a_0) \right\} \right.$$

$$+ (1/r_2)\exp(ik_0 r_2) \left\{ 1 - \exp(-r_2/a_0) \right\} \qquad x$$

$$\left. \left\{ A + B \exp(-r_2/a_0) + (Cr_{12}/a_0) \exp(-r_2/a_0) \right\} \right] , \qquad (57)$$

we have examined the contributions of the various terms to the scattering by carrying out the cross section calculations with trial functions using various combinations of the five parameters in (57). In Figures 2, 3, and 4, the results of the various calculations are graphed. It is evident that the parameter b or c alone (Fig. 2) is not sufficient. Both b and c are required to give a good fit to the experimental data at small angles. The effect of the parameters A, B, and C is to raise the cross section curve at large angles (Figs. 3, 4). When A alone is used, the curve (Fig. 3) is raised at large angles; when A is used in combination with either b or c, or with b and c, no effect of A at large angles is evident. As the number of parameters in the scattered wave part of the trial function is increased, the rise of the scattering curve af large angles also increases (Fig. 4). Since the parameters in the incident wave part of the trial function serve not only to improve the theoretical results at small angles but also to cut down the effectiveness of the parameters in the scattered wave part for raising the theoretical curve at large angles, we feel that a trial function employing all five parameters will provide improvement

Fig. 3. The theoretical cross sections for the elastic scattering of 350 volt electrons by hydrogen atoms calculated by the linear variational method employing the trial functions (44), (45) with the parameter A (b, c = 0), with the parameters A, b (c = 0), and with the parameters A, c (b = 0) compared with those obtained using the parameters A, b, c in the same trial function. Ordinate, Elastic scattering cross section in units of 10^{-18} cm.^{2} Abscissa, Angle θ through which the scattering takes place.
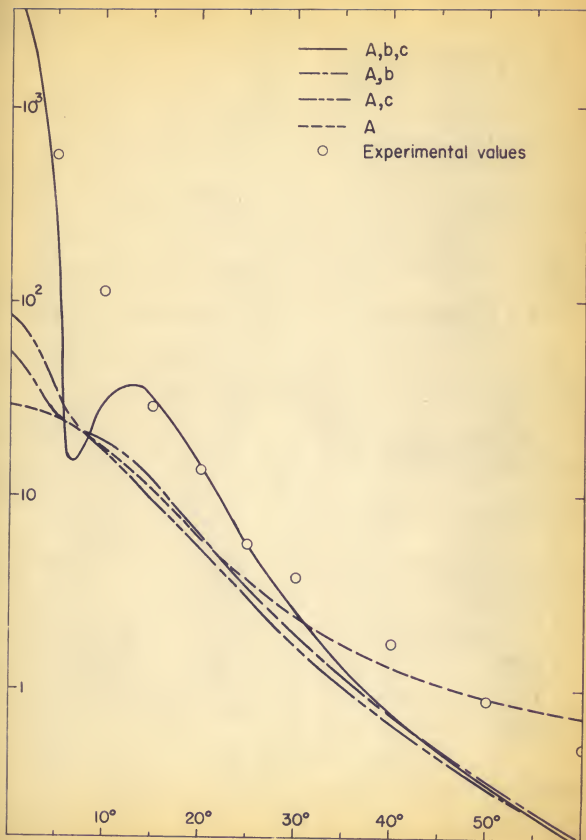
Fig. 4. The cross sections for the elastic scattering of 350 volt electrons by hydrogen atoms calculated by the linear variational procedure employing the trial function (57) with the parameters A, b, B (c, C = 0) and with the parameters A, B, C (b, c = 0) are compared to those obtained employing the same trial functions with the parameters A, b, c (B, C = 0). Ordinate, Elastic scattering cross sections in units of 10^{-18} cm.^{2} Abscissa, Angle Θ through which the scattering takes place.

Legend:
— A, b, c
—·— A, B, C
- - - A, b, B
○ Experimental values
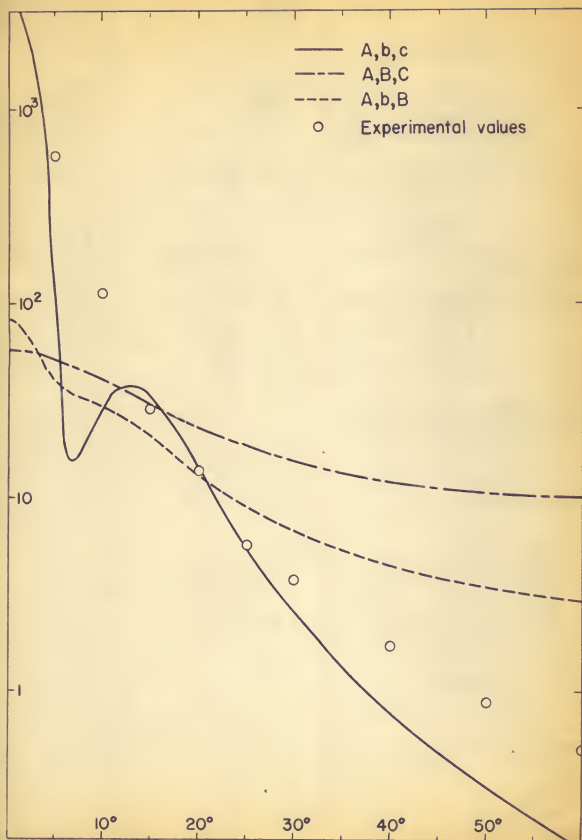
of the Born approximation over the entire angular range of the
scattering.

V. CONCLUSIONS

The success of wave mechanics in explaining phenomena beyond the realm of classical physics has been unqualified. A major theoretical problem is resolving the frustration of not knowing the wave function which applies to a particular problem. In the event that a relatively simple asymptotic form of the wave function is known, however, a variational procedure may sometimes be employed to provide a solution to the problem without possessing the exact wave function. Since the complete set of hydrogen eigenfunctions is known, the variational method outlined in Part II should be useful in obtaining inelastic, as well as elastic, cross sections for the scattering of electrons by hydrogen without going into partial wave analyses as is usually done.[20] Only the elastic scattering at high velocities of impact has been considered here to illustrate the method. The simple form of our trial function accounts for the distortion and polarization effects expected to become important as the impact velocity or scattering angle decreases to where the Born approximation is inadequate. The deviation of our theoretical curves from the observed scattering cross sections at large angles remains when the number

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[20] A variational method, using partial waves, for obtaining inelastic cross sections has been derived by: B. L. Moiseiwitsch, Phys. Rev. **82**, 753 (1951).

of adjustable parameters is limited to three. If the number of param-
eters could be increased to perhaps five, thereby greatly increasing
the labor of calculations, an extension of the improvement of the Born
approximation in the large angle direction could probably be realized.
Since the departures of theoretical from experimental curves are of
much larger magnitude in the small angle region than in the large
angle region, the three parameter linear variational procedure given
here is considered to be a satisfactory improvement of the Born
approximation in providing a theoretical basis for the elastic scattering
of electrons by hydrogen atoms at high velocities of impact.

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BIOGRAPHICAL SKETCH

June Grimm Jones was born in Wheeling, West Virginia, on October 16, 1918. She was awarded the A. B. degree in mathematics and physics by West Virginia University in 1938. After her undergraduate work, she was on the actuarial staff of Acacia Mutual Life Insurance Company located in Washington, D. C. until December, 1940 when she resigned to accompany her husband, Mark Wallon Jones, on an assignment in South America. Upon her return to the United States, she enrolled in the graduate school of the University of Florida in the summer of 1947. She was granted the Master of Science degree in June, 1948, by the Department of Physics. The following two years, she was an assistant member of the research staff of the Geophysical Institute located in College, Alaska. In September, 1950, she returned to the University of Florida to pursue studies in theoretical physics leading to the degree of Doctor of Philosophy. She is a member of Phi Beta Kappa, Phi Kappa Phi, Sigma Pi Sigma, Sigma Xi, and Kappa Kappa Gamma social fraternity.

This dissertation was prepared under the direction of the co-chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

June 8, 1953

Dean, College of Arts and Sciences

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